# **EXHIBIT 33**

August 1, 2018



REBUTTAL REPORT OF PHILIP K. HOPKE, PH.D.

PRESENTED BY: PHILIP K. HOPKE, MANAGING PARTNER

9372 KIRK ROAD, WESTERNVILLE, NY 13420

# REBUTTAL REPORT OF PHILIP K. HOPKE, PH.D.

The following are opinions expressed by Mr. Lyle Chinkin concerning my expert report in support of Class Certification. I rebut each of these below.

#### 1. CHINKIN OPINIONS 1 THROUGH 4

OPINION 1: Dr. Hopke's initial assumptions and assertions contained in his expert report regarding the acid-base chemistry and pH of the PTFE dispersion solution, APFO, and PFOA are incorrect and unreliable.

OPINION 2: Dr. Hopke's initial claim contained in his expert report(s) that essentially all APFO will convert to PFOA, be volatilized, and emitted as PFOA particulate matter is unsupported and incorrect.

OPINION 3: Dr. Hopke's initial assertions contained in his expert report(s) regarding the thermal dissociation and decomposition of APFO and PFOA are counter to the peer-reviewed published papers Hopke relied on and are unsupported and unreliable.

OPINION 4: Dr. Hopke's new assertion (as stated for the first time during his deposition) that APFO sublimates then dissociates to form PFOA is contrary to his claims in his expert report, is based on a tenuous computational simulation of another chemical compound and cannot be tested using existing scientific measurements

In my expert report in support of class certification (September 1, 2017), I described the volatilization of PFOA from the coated cloth in the Saint Gobain heated towers in relatively simple terms to make it understandable to the judge and jury. Mr. Chinkin has taken issue with this description and with my deposition testimony about these opinions, which makes it necessary for me to provide a detailed discussion of the chemistry that occurred in the coating operations.

#### **SUBLIMATION**

Sublimation is the process of material moving directly from solid to a gas without passing through the liquid phase. It is a surface phenomenon, so surface-to-volume ratio of the material is important. Ammonium Perfluorooctanoate ("APFO") is a solid that sublimes very weakly at room temperature. However, salts do not directly sublime. In order to sublime, APFO has to undergo a multiple step mechanism (Zhu et al., 2006) in which an H+ moves from the ammonium ion to the PFO- forming ammonia and Perfluorooctanoic Acid ("PFOA"). They then can move into the gas phase. Drying the dispersion solution will produce very small crystals on the surface of the cloth fibers or the PTFE particles. Sublimation then occurs from the surface of those crystals. The reaction pathway can be described schematically as follows:

 $NH_4^+C_7F_{15}COO^-(s) \Rightarrow NH_3 --HOOCC_7F_{15}(a) \Rightarrow NH_3(a) + PFOA(a) \Rightarrow NH_3(g) + PFOA(g)$ 

Where (s) represents the solid crystals, (a) represent material on the crystal surface, and (g) represents the gas phase. This equation represents a series of equilibria, but in the process, there is active transport of material from the fabric to the exhaust stacks in order to move the water from the fabric and thus force it to dry. This air movement will remove the gaseous components (ammonia and PFOA) so as to drive the reaction chain to the right.

This process is slow at room temperature, but it increases as the temperature increases. Thus, a key issue is the relative rate of dissociation compared to decomposition of the PFOA by

decarboxylation. Decarboxylation comes from breaking of the carbon-carbon bond between the carboxyl acid carbon and the adjacent carbon with 2 F atoms attached. Decarboxylation will only occur in PFOA. It will not occur in crystalline APFO where the ammonium ion is ionically bonded to the carboxy acid ion. The presence of the ammonium ion makes the "leaving group" too heavy to allow the internal atomic motion needed to proceed to the breaking of the carboncarbon bond. Krusic and Roe (2004) claim to decompose APFO by sealing it in a glass vial and heating it to temperatures greater than or equal to 190°C. However, most of the experiments on decomposition of perfluorooctanoic moieties do so in solution. Decarboxylation in the treatment of PFOA in solution is typically done using catalytic materials such as TiO<sub>2</sub> (Dilbert et al., 2007) or In<sub>2</sub>O<sub>3</sub> (Li et al., 2013) in the presence of high energy light. Li et al. (2013) state "Because of its high stability, there is no known natural decomposition processes and most conventional techniques including biological degradation, oxidation and reduction are also not effective to destruct PFOA under mild conditions." Alternatively, strong oxidizers like activated persulfate (Yin et al., 2016) can be used to decompose PFOA. Thus, simple heating of PFOA in air is unlikely to be effective in causing rapid decarboxylation. Krusic et al. (2005) showed very slow decomposition in quartz. In the Krusic experiments, the material was confined to the reaction vessel and could not move from the areas of higher temperature into the exhaust ducts as would have occurred under normal plant operations at the Saint-Gobain/ChemFab plants. Mr. Chinkin's expert report confirms that APFO sublimes at 130°C, a temperature at which it will not decompose. Since sublimation clearly occurs at temperatures below the 163°C decomposition temperature, it is clear that the dissociation requires less energy than the decarboxylation, and dissociation and sublimation will occur prior to decomposition.

The vapor pressure increases from very low values at room temperature as the temperature rises such that at 100°C (212°F), it is estimated to be 4.5 Pa based on Equation 7 in Barton et al. (2009):

$$\ln(p/Pa) = \frac{-10695}{T} + 37.292$$

The vapor pressure rises to a moderate value of 143 Pa at 150°C (302°F) which is the upper range of temperatures indicated for the drying area of the towers. As the solution dries, the APFO will form small crystals with a high surface to volume ratio such that there is a substantial opportunity for the APFO to dissociate and sublime. As the dried material moves to even higher temperatures, sublimation will become more rapid.

Mr. Chinkin's opinions are based on the failure of PFO- ion to volatilize from the solution. However, that is not the mechanism on which my opinion is based. As the material dries, it "precipitates" as noted by Mr. Chinkin. However, to nucleate and form a crystal, there needs to be a site to nucleate on once the solution exceeds its solubility product. These sites will be locations on the Teflon particles or on the fibers. In both cases, the solution will be a thin layer on the fibers and not a bulk solution as would exist in a container. The mass transfer of water molecules into the air during the drying process will occur simultaneously with the transfer of the gaseous end products of the reaction chain presented previously. Thus, it is my opinion that the APFO dissociates to PFOA, sublimes, and then is fully released into the wet gas exhausted from the drying process without decomposition since sublimation is clearly favored over decomposition at the lower temperatures in the drying area.

The process described in the original report and the deposition is really presenting the same concepts. In the deposition I described it in more detail since it had been overly simplified and needed to be more detailed as outlined above. The mechanism of dissociation is just as critical to the assertion of decomposition as it is to sublimation. However, the sublimation process has been demonstrated in the laboratory (Barton et al., 2009), but the decomposition in time frame of

seconds without the presence of a catalytic surface, such as the glass in the Krusic et al. experiments, has not been demonstrated.

The following are my responses to the other Chinkin opinions:

#### 2. CHINKIN OPINION 5

<u>OPINION 5:</u> Dr. Hopke's opinion that the PFOA emissions from both facilities were completely uncontrolled is unsupported and incorrect.

If the chemistry is properly understood, it is clear that PFOA will be formed by the dissociation of the APFO on the surface of the microcrystals formed by drying the coating solution. The PFOA will sublime before it can decompose, go into the exhaust stream, and will not be decomposed by the abaters since it will be attached to the particles in the exhaust stream and they will not be removed by the abaters. Saint-Gobain recognized the failure of abaters to remove PFOA, as evidenced by the testing of a filtration system to remove particles in the Merrimack plant instead of trying to decompose the PFOA with abaters.

#### 3. CHINKIN OPINION 6

OPINION 6: Dr. Hopke's overall PFOA emissions assessment estimates are incorrect and arbitrary.

In my report of last September, I used a Saint-Gobain spreadsheet produced in discovery that was prepared by the company to calculate the PFOA emissions for the North Bennington plant based upon annual PFOA-containing dispersion usage. The spreadsheet, which I attached to my report, clearly indicated that it was calculating PFOA emissions based upon 100% of the APFO contained in the dispersions used. The calculations were performed in October 2001, so it is reasonable to assume the usage data was current at that time. As I stated in my report, the APFO emissions calculated in the spreadsheet for North Bennington were nearly 7,000 pounds per year (6,946). In this spreadsheet, the Algoflon D3312 dispersion did not identify the surfactant contained as APFO, but we know from other documents that it was. I did not use the spreadsheet I was questioned about in my deposition to calculate the emissions in my report (Ex. 20).

# 4. CHINKIN OPINION 7

OPINION 7: Dr. Hopke's overall assessment is incomplete given his assumption that all of the PFOA in the environment in Bennington was emitted solely into the air from the two Chemfab facilities.

These opinions are clearly incorrect, since as demonstrated above, Mr. Chinkin clearly did not understand the critical phase (solid) that he indicates does form (precipitate) and the necessity of dissociation to support their false hypothesis of decomposition under the relatively mild chemical conditions that occurred in the plant.

#### SOURCE APPORTIONMENT

Mr. Chinkin criticizes my report because it did not utilize source apportionment methods to look for multiple sources of PFOA in the North Bennington area. However, there has been no credible evidence of the existence of other sources of PFOA that would have been distributed spatially across the domain in which the contaminated wells were found. His report indicates that he identified "other potential sources". He indicates that industrial sources have been in existence

since the early 1900s, but PFOA was not manufactured and used until at least 1948. The Barr report describes other "potential" sources that can only be sources through disposal of wastes in the local landfalls. However, the distribution of contamination is clearly related to atmospheric deposition from the only known atmospheric source of PFOA.

Furthermore, he comments that: "Barr's recent work also confirms that there are background local, regional, and global sources of PFOA other than the former ChemFab facilities that have not been accounted for in air deposition modeling for the Bennington area." However, the Barr report only lists possible sources without any measurements or other information that "confirms" other sources. In the documents provided by Mr. Chinkin in response to the subpoena for all documents related to his report, no documents were provided that discussed other sources of PFOA. Thus, Mr. Chinkin's contention that there had to be other sources of PFOA is unfounded and entirely speculative.

The application of source apportionment methods requires some basic assumptions to be met. These assumptions include that each source have a unique profile that remains constant over time and that there are a sufficient number of measured species that are greater than the number of sources. In this case, there were multiple formulations used in the ChemFab facility and a variety of unknown mixtures in the other potential sources. In addition, there is very likely to have been differential adsorption of the various species in the surficial soils depending on the amount and types of organic matter across the region. Thus, it is highly unlikely that the system would meet the stationarity assumptions on which receptor models are based. As noted in the Vermont DEC's February 21, 2018 comments on the December 2017 version of the Barr report, "The SI report states the chemical signature from air emissions from Chemfab is no longer distinguishable in soil data." and "The SI report states a preliminary multivariate analysis (MVA) did not yield results from which distinct signatures of other potential sources could be readily identified. This statement seems to contradict Barr's assertion that other sources are a possible cause of contamination." Thus, there is no basis for applying source apportionment methods to the data.

Finally, I also rely on the rebuttal opinion of Dr. Don Siegel regarding the lack of evidence of other sources. Dr. Siegel discusses recent sampling of the Saint-Gobain Water Street plant where residues of perfluorooctane sulfonate ("PFOS") were found in high concentrations including in the remaining emissions stacks. These results show that ChemFab/Saint-Gobain is the likely source of the low levels of PFOS in groundwater (relative to PFOA) in some wells in the Bennington area. Mr. Chinkin's reliance on Barr and Golder for the opinion that the presence of PFOS is an indication of other sources of PFOA is invalid.

# 5. REBUTTAL OF OPINIONS OF FELIX W. FLECHAS, P.E.

My opinions about the failure of the ChemFab/Saint-Gobain facilities to comply with Vermont air pollution regulations were addressed by Mr. Felix Flechas. Mr. David Mears, J.D., former Commissioner of the Vermont Department of Environmental Conservation, will rebut Mr. Flechas' opinions. I will note that Mr. Flechas offered no scientific opinions about whether ChemFab/Saint-Gobain knew or should have known about its emissions of PFOA or whether the company failed to utilize available control technologies for control of its emissions of PFOA. From my review of his resume, it is unlikely he would be qualified to do so.

# 6. REFERENCES

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